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## (54) SOLID POLYMER TYPE FUEL CELL AND MANUFACTURE THEREOF

(57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a voltage stable with age by correcting unevenness in contained water distribution.

**SOLUTION:** This fuel cell is provided with a solid polymer electrolyte membrane 3, an anode catalyst layer 2a and a cathode catalyst layer 2b placed on the both sides of the solid polymer electrolyte membrane 3, and an anode gas diffusion layer 1a and a cathode gas diffusion layer 1b individually placed on surfaces opposite to surfaces on which the catalyst layers 2a, 2b are in contact with the solid polymer electrolyte membrane 3. The average porous diameter of at least one porous layer forming the anode gas diffusion layer 1a is smaller than the average porous diameter of a porous layer forming the cathode gas diffusion layer 1b.



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CLAIMS

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[Claim(s)]

[Claim 1] The solid-state polyelectrolyte film, and the anode catalyst bed and cathode catalyst bed arranged to both sides of this solid-state polyelectrolyte film, In the polymer electrolyte fuel cell equipped with the anode gas diffusion layer and cathode gaseous diffusion layer which are arranged in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds, respectively, and are formed by the porous layer The average pore diameter of at least one porous layer which forms said anode gas diffusion layer is a polymer electrolyte fuel cell characterized by being smaller than the average pore diameter of the porous layer which forms said cathode gaseous diffusion layer.

[Claim 2] The average pore diameter of the part located in the reactant-gas downstream of said gaseous-diffusion layer in the polymer electrolyte fuel cell equipped with the gaseous-diffusion layer of the couple which is arranged in the solid-state polyelectrolyte film, the catalyst bed of the couple arranged to both sides of this solid-state polyelectrolyte film, and the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds, and is formed by the porous layer is the polymer electrolyte fuel cell characterized by to be larger than the average pore diameter of the part located in the reactant-gas upstream section.

[Claim 3] The solid-state polyelectrolyte film and the catalyst bed of the couple arranged to both sides of this solid-state polyelectrolyte film, The cell which has the gaseous diffusion layer of the couple which is arranged in the field of objection of the field which touches said solid-state polyelectrolyte film, and is formed by the porous layer In the polymer electrolyte fuel cell constituted as a layered product which carried out two or more laminatings through the gas impermeable separator which has a reactant gas supply function The average pore diameter of the porous layer which forms the gaseous diffusion layer of at least 1 cel located in the edge of said layered product is a polymer electrolyte fuel cell characterized by being larger than the average pore diameter of the porous layer which forms the gaseous diffusion layer of the cel of the center section of said layered product.

[Claim 4] The polymer electrolyte fuel cell according to claim 1 to 3 characterized by 90% or more of the pore of the porous layer which touches a catalyst bed consisting of pore diameters of 10 micrometers or less.

[Claim 5] The polymer electrolyte fuel cell according to claim 1 to 4 characterized by making the porosity of the porous layer which touches a catalyst bed 70% or more.

[Claim 6] An anode catalyst bed and a cathode catalyst bed are joined to both sides of the solid-state polyelectrolyte film. In the manufacture approach of the polymer electrolyte fuel cell which joins the anode gas diffusion layer and cathode gaseous diffusion layer which are formed in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds by the porous layer, respectively After said anode gas diffusion layer applies the ink which becomes a carbon porous body from a carbon particle and a fluorocarbon-resin-dispersion object at least so that a spreading side may touch a catalyst bed, While heat-treating and forming above the glass transition temperature of a fluororesin, said cathode gaseous diffusion layer The manufacture approach of the polymer electrolyte fuel cell characterized by heat-treating and forming them above the glass transition temperature of a fluororesin after applying the fine particles which turn into a carbon porous body from a carbon particle and a fluororesin particle at least so that a spreading side may touch a catalyst bed.

[Claim 7] The manufacture approach of the polymer electrolyte fuel cell according to claim 6 characterized by making the weight rate of fluororesin solid content 65% or less to the sum total weight of a carbon particle and fluororesin solid content.

[Claim 8] In the manufacture approach of the polymer electrolyte fuel cell which joins the catalyst bed of a

couple to both sides of the solid-state polyelectrolyte film, and joins the gaseous diffusion layer of the couple formed in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds by the porous layer Into the part located in the reactant gas upstream section of said gaseous diffusion layer After applying the ink which becomes a carbon porous body from a carbon particle and a fluorocarbon-resin-dispersion object at least so that a spreading side may touch a catalyst bed, While heat-treating and forming above the glass transition temperature of a fluororesin, into the part located in a reactant gas downstream The manufacture approach of the polymer electrolyte fuel cell characterized by heat-treating and forming them above the glass transition temperature of a fluororesin after applying the fine particles which turn into a carbon porous body from a carbon particle and a fluororesin at least so that a spreading side may touch a catalyst bed.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the polymer electrolyte fuel cell which optimized the pore diameter of a gaseous diffusion layer, and its manufacture approach.

[0002]

[Description of the Prior Art] Generally, a fuel cell is equipment which carries out direct conversion of the chemical energy which the above-mentioned fuel has to electrical energy by making fuels, such as hydrogen, and oxidizers, such as air, react electrochemically. Moreover, a fuel cell is classified into a thing various type according to the difference in an electrolyte etc., and the polymer electrolyte fuel cell which used the solid-state polyelectrolyte film for the electrolyte as one is known.

[0003] Drawing 13 is the sectional view showing the configuration of the conventional polymer electrolyte fuel cell. As shown in drawing 13, the conventional polymer electrolyte fuel cell possesses the separator 5 of gas impermeability which has a slot for supplying reactant gas to each of the cell 4 which made the solid-state polyelectrolyte film 3 which has ion conductivity and gas isolation pinch, anode gas diffusion layer 1a which is an electrode, and cathode gaseous diffusion layer 1b through catalyst bed 2a set to anode gas diffusion layer 1a and cathode gaseous diffusion layer 1b from Pt etc., respectively, and 2b, and is constituted.

[0004] And if fuels, such as hydrogen, are supplied to anode gas diffusion layer 1a and oxidizers, such as air, are supplied to cathode gaseous diffusion layer 1b, respectively, electromotive force will arise in a cell 4 according to electrochemical reaction. The electromotive force of this cell 4 is used as a cell stack which usually carried out the laminating of two or more cells 4 to about 1V at most since it was low. Since this electrochemical reaction is exothermic reaction, in order to remove surplus heat, the cooling plate 7 which circulates a refrigerant every cell layered product 6 which carried out two or more laminatings of the cell 4 through the separator 5 is inserted.

[0005] Moreover, since the gas leak to the outside of a system has the danger of explosion by combustible gas, such as decline in the rate of gas utilization, and hydrogen, the gas seal of between the solid-state polyelectrolyte film 3 and a separator 5 is carried out through the sealing compound 8.

[0006] The perfluoro sulfonic-acid film which is for example, fluorine system ion exchange membrane is used for the solid-state polyelectrolyte film 3, and these solid-state polyelectrolyte film 3 functions on it as an electrolyte by having and carrying out the water of the exchange group of a hydrogen ion into a molecule. However, if there is little moisture content of a cell, since the ion conductivity of the solid-state polyelectrolyte film 3 will get worse and the function as an electrolyte will fall remarkably, the cell engine performance falls. On the other hand, if the moisture content of a cell becomes superfluous at reverse, since water will condense in the cell reaction section and supply of the gas to the cell reaction section will be checked, the cell engine performance falls similarly.

[0007] By the way, in cathode gaseous diffusion layer 1b, since water is generated in connection with electrode reaction, there is much moisture content and the relative humidity of reactant gas is also higher than anode gas diffusion layer 1a. Moreover, since a part of water generated by cathode gaseous diffusion layer 1b moves also to anode gas diffusion layer 1a and these moisture is carried out in part by reactant gas, the direction of the lower stream of a river of reactant gas has high relative humidity as compared with the upstream.

[0008] That is, distribution has arisen in the relative humidity of reactant gas on anode gas diffusion layer 1a, cathode gaseous diffusion layer 1b, or the upstream and the lower stream of a river of reactant gas. Thus, with the field interior division cloth of the relative humidity of the reactant gas produced in the cell flat

surface, field interior division cloth is generated in the moisture content of the electrode reaction sections, such as a catalyst bed and an electrolyte membrane, [ in a cell flat surface ].

[0009] Consequently, since reaction surface area falls with lowering of an electrolyte function in a part with little moisture content while gaseous diffusion nature gets worse by condensation of water in a part with superfluous moisture content, ununiformity-ization within a field of current density arises and the cell engine performance falls.

[0010] Therefore, in order to prevent cell performance degradation, it is necessary to make it distribution of the relative humidity in the upstream and the lower stream of a river of reactant gas not cause the field interior division cloth of the moisture content of a catalyst bed or an electrolyte membrane. What gave work as shock absorbing material which does not make the moisture content of the catalyst bed to which electrode reaction is performed according to distribution of the relative humidity of reactant gas, or an electrolyte membrane produce distribution by preparing a layer with many rates of pore with a pore diameter smaller than a carbon porous body in the field which touches the catalyst bed of the carbon porous body with the large pore diameter usually used for the gaseous diffusion layer as the example is thought out.

[0011]

[Problem(s) to be Solved by the Invention] However, in the conventional example mentioned above, if the long duration generation of electrical energy is performed, distribution will also produce the electrode reaction section in the moisture content within a cell side gradually with the field interior division cloth of the difference in the relative humidity of anode gas diffusion layer 1a and cathode gaseous diffusion layer 1b, or the relative humidity of the reactant gas resulting from the difference in the relative humidity in the upstream and the lower stream of a river of reactant gas. Since lowering of the reaction area accompanying the electrolyte performance degradation by lowering and desiccation of the gaseous diffusion nature by condensation of water arises and ununiformity-ization of current density occurs with the cell side interior division cloth of the moisture content in this electrode reaction section, the technical problem that cell voltage falls occurs.

[0012] Cell temperature is lower than the cel located in a center section on the other hand since heat release has more cels located in an edge at a fuel cell stack, and relative humidity is high. Therefore, the cel located in an edge also has the technical problem that cell voltage is lower than the cel of a center section, by lowering of the gaseous diffusion function by condensation of water.

[0013] Then, it is in offering the highly efficient polymer electrolyte fuel cell with which the electrical potential difference stabilized with time is obtained, and its manufacture approach by having made this invention in consideration of the above-mentioned situation, being optimizing the pore diameter of the gaseous diffusion layer for polymer electrolyte fuel cells, and producing it according to distribution of the relative humidity of the reactant gas which had become a technical problem conventionally, and correcting ununiformity-ization of the moisture content distribution of the cell reaction section produced with time.

[0014]

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, then, a polymer electrolyte fuel cell according to claim 1 The solid-state polyelectrolyte film, and the anode catalyst bed and cathode catalyst bed arranged to both sides of this solid-state polyelectrolyte film, In the polymer electrolyte fuel cell equipped with the anode gas diffusion layer and cathode gaseous diffusion layer which are arranged in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds, respectively, and are formed by the porous layer The average pore diameter of at least one porous layer which forms said anode gas diffusion layer is characterized by being smaller than the average pore diameter of the porous layer which forms said cathode gaseous diffusion layer.

[0015] Since the amount of the moisture which the amount of the moisture relatively discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section of an anode with little moisture content decreases, and is relatively discharged with reactant gas through a gaseous diffusion layer by the configuration of a polymer electrolyte fuel cell according to claim 1 from the electrode reaction section of a cathode with much moisture content increases, the field interior division cloth of the moisture content of the electrode reaction section is controlled.

[0016] The catalyst bed of the couple which has arranged the polymer electrolyte fuel cell according to claim 2 to both sides of the solid-state polyelectrolyte film and this solid-state polyelectrolyte film, In the polymer electrolyte fuel cell equipped with the gaseous diffusion layer of the couple which is arranged in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds, and is formed by the porous layer The average pore diameter of the part located in the reactant gas downstream of said gaseous diffusion layer is characterized by being larger than the average pore diameter

of the part located in the reactant gas upstream section.

[0017] Since the amount of the moisture which the amount of the moisture relatively discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section in the reactant gas upstream section with little moisture content decreases, and is relatively discharged with reactant gas through a gaseous diffusion layer by the configuration of a polymer electrolyte fuel cell according to claim 2 from the electrode reaction section by the reactant gas downstream with much moisture content increases, the field interior division cloth of the moisture content of the electrode reaction section is controlled.

[0018] The catalyst bed of the couple which has arranged the polymer electrolyte fuel cell according to claim 3 to both sides of the solid-state polyelectrolyte film and this solid-state polyelectrolyte film, The cell which has the gaseous diffusion layer of the couple which is arranged in the field of objection of the field which touches said solid-state polyelectrolyte film, and is formed by the porous layer In the polymer electrolyte fuel cell constituted as a layered product which carried out two or more laminatings through the gas impermeable separator which has a reactant gas supply function The average pore diameter of the porous layer which forms the gaseous diffusion layer of at least 1 cel located in the edge of said layered product is characterized by being larger than the average pore diameter of the porous layer which forms the gaseous diffusion layer of the cel of the center section of said layered product.

[0019] In the cel of a layered product edge, by heat dissipation, compared with the cel located in a center section, temperature is low, and relative humidity becomes high. Therefore, in the cel of an edge, gaseous diffusion nature falls by condensation of water. By the configuration of a polymer electrolyte fuel cell according to claim 3, in the cel of a layered product edge, since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section increases, gaseous diffusion nature improves.

[0020] A polymer electrolyte fuel cell according to claim 4 is characterized by 90% or more of the pore of the porous layer which touches a catalyst bed according to claim 1 to 3 consisting of pore diameters of 10 micrometers or less.

[0021] Since the movement magnitude of moisture decreases between reactant gas and the electrode reaction section, by the configuration of a polymer electrolyte fuel cell according to claim 4 in the field where the relative humidity of reactant gas is low Since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section decreases and the amount of the moisture supplied to the electrode reaction section decreases in the field where the relative humidity of reactant gas is high, the field interior division cloth of the moisture content of the electrode reaction section produced with the field interior division cloth of the relative humidity of reactant gas is eased.

[0022] A polymer electrolyte fuel cell according to claim 5 is characterized by making the porosity of the porous layer which touches a catalyst bed according to claim 1 to 4 70% or more.

[0023] According to the polymer electrolyte fuel cell according to claim 5, lowering of the gaseous diffusion function of a gaseous diffusion layer can be prevented.

[0024] The manufacture approach of a polymer electrolyte fuel cell according to claim 6 An anode catalyst bed and a cathode catalyst bed are joined to both sides of the solid-state polyelectrolyte film. In the manufacture approach of the polymer electrolyte fuel cell which joins the anode gas diffusion layer and cathode gaseous diffusion layer which are formed in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds by the porous layer, respectively After said anode gas diffusion layer applies the ink which becomes a carbon porous body from a carbon particle and a fluorocarbon-resin-dispersion object at least so that a spreading side may touch a catalyst bed, While heat-treating and forming above the glass transition temperature of a fluororesin, said cathode gaseous diffusion layer It is characterized by heat-treating and forming them above the glass transition temperature of a fluororesin, after applying the fine particles which turn into a carbon porous body from a carbon particle and a fluororesin particle at least so that a spreading side may touch a catalyst bed.

[0025] According to the manufacture approach of a polymer electrolyte fuel cell according to claim 6, an average pore diameter becomes small rather than the porous layer to which the porous layer which touches a catalyst bed among anode gas diffusion layers touches a catalyst bed among cathode diffusion layers.

[0026] The manufacture approach of a polymer electrolyte fuel cell according to claim 7 is characterized by making the weight rate of fluororesin solid content according to claim 6 65% or less to the sum total weight of a carbon particle and fluororesin solid content.

[0027] According to the manufacture approach of a polymer electrolyte fuel cell according to claim 7, the porosity of a gaseous diffusion layer becomes 70% or more.

[0028] The manufacture approach of a polymer electrolyte fuel cell according to claim 8 In the manufacture

approach of the polymer electrolyte fuel cell which joins the catalyst bed of a couple to both sides of the solid-state polyelectrolyte film, and joins the gaseous diffusion layer of the couple formed in the field of objection of the field which touches said solid-state polyelectrolyte film of these catalyst beds by the porous layer into the part located in the reactant gas upstream section of said gaseous diffusion layer. After applying the ink which becomes a carbon porous body from a carbon particle and a fluorocarbon-resin-dispersion object at least so that a spreading side may touch a catalyst bed, while heat-treating and forming above the glass transition temperature of a fluororesin, into the part located in a reactant gas downstream. It is characterized by heat-treating and forming them above the glass transition temperature of a fluororesin, after applying the fine particles which turn into a carbon porous body from a carbon particle and a fluororesin at least so that a spreading side may touch a catalyst bed.

[0029] According to the manufacture approach of a polymer electrolyte fuel cell according to claim 8, an average pore diameter becomes large rather than the part to which the part located in the reactant gas downstream of the porous layer which touches a catalyst bed among gaseous diffusion layers is located in the reactant gas upstream section.

[0030]

[Embodiment of the Invention] Hereafter, the operation gestalt of this invention is concretely explained with reference to a drawing. In addition, it explains using the sign same into a corresponding part identically to the conventional configuration as drawing 13.

[0031] [1st operation gestalt] drawing 1 is the sectional view showing the 1st operation gestalt of the polymer electrolyte fuel cell concerning this invention.

[0032] As shown in drawing 1, the cell 4 consists of anode gas diffusion layer 1a and cathode gaseous diffusion layer 1b which a polymer electrolyte fuel cell is arranged in the field of objection of the field which touches the solid-state polyelectrolyte film 3 of the solid-state polyelectrolyte film 3, anode catalyst bed 2a and cathode catalyst bed 2b which have been arranged to both sides of this solid-state polyelectrolyte film 3, and these catalyst bed 2a and 2b, respectively, and are formed by the porous layer. In addition, since other configurations of the polymer electrolyte fuel cell of this operation gestalt are the same as that of drawing 13, the explanation is omitted.

[0033] Anode gas diffusion layer 1a consists of two-layer porous layers of carbon paper 1c (270 micrometers in thickness), and 1d of carbon layers. After 1d of this anode carbon layer applied the ink which mixed a carbon particle (VulcanXC-72R), polytetrafluoroethylene dispersion (dispersing element) (TFE30), a surface active agent, and pure water on carbon paper 1c using the screen printer, it formed by performing heat treatment for 15 minutes at 350 degrees C.

[0034] On the other hand, cathode gaseous diffusion layer 1b consists of two-layer porous layers of carbon paper 1c and cathode carbon layer 1e. This cathode carbon layer 1e formed by performing heat treatment for 15 minutes at 350 degrees C, after applying the fine particles which mixed a carbon particle (VulcanXC-72R) and polytetrafluoroethylene powder (TFE60) on carbon paper 1c.

[0035] Drawing 2 shows pore diameter distribution of 1d of anode carbon layers and cathode carbon layer 1e when making the content of polytetrafluoroethylene into 35%. Although the cathode carbon layer 1e has a pore diameter larger than 1d of anode carbon layers, there are many rates, and the average pore diameter is large. Here, 90% or more consists of pores 10 micrometers or less, and, as for each of 1d of anode carbon layers, and cathode carbon layer 1e, that from which porosity becomes about 80% was obtained.

[0036] Next, anode catalyst bed 2a was formed on 1d of anode carbon layers, and cathode catalyst bed 2b was formed on cathode carbon layer 1e, respectively, and the solid-state polyelectrolyte film 3 was made to pinch, it joined, and the cell 4 was created as mentioned above.

[0037] Thus, in the polymer electrolyte fuel cell of this operation gestalt, the average pore diameter of at least one porous layer which forms anode gas diffusion layer 1a is made smaller than the average pore diameter of the porous layer which forms cathode gaseous diffusion layer 1b.

[0038] as mentioned above, by the manufacture approach of the polymer electrolyte fuel cell of this operation gestalt. After anode gas diffusion layer 1a applies the ink which becomes a carbon porous body from a carbon particle and a fluorocarbon-resin-dispersion object at least so that a spreading side may touch a catalyst bed, while heat-treating and forming above the glass transition temperature of a fluororesin, cathode gaseous diffusion layer 1b. After applying the fine particles which turn into a carbon porous body from a carbon particle and a fluororesin particle at least so that a spreading side may touch a catalyst bed, they are heat-treated and formed above the glass transition temperature of a fluororesin.

[0039] Next, an operation and effectiveness of this operation gestalt are explained.

[0040] In the polymer electrolyte fuel cell of this operation gestalt, since the average pore diameter of 1d of

anode carbon layers is small compared with the average pore diameter of cathode carbon layer 1e The amount of the moisture discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section of an anode with little moisture content decreases. Since the amount of the moisture relatively discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section of a cathode with much moisture content increases, the field interior division cloth of the moisture content of the electrode reaction section is eased.

[0041] About the polymer electrolyte fuel cell of this operation gestalt, the generation-of-electrical-energy trial was performed at the operating temperature of 80 degrees C, operating pressure 0.1MPa, current density 400 mA/cm<sup>2</sup>, the anode humidification temperature of 70 degrees C, the cathode humidification temperature of 70 degrees C, 70% of rates of hydrogen gas utilization, and 40% of air gas utilization factors. Here, in order to compare with the cell of this operation gestalt, the cell which changed only the specification of a carbon layer was created and the generation-of-electrical-energy trial was performed on the same conditions. It is shown as examples 1 and 2 of a comparison below.

[0042] The cell of the example 1 of a comparison is a cell using the thing of the specification same as an anode carbon layer and a cathode carbon layer as the cathode carbon layer in this operation gestalt. That is, the cell of the example 1 of a comparison is a cell by which it was made for pore diameter distribution of an anode and a cathode to become equal.

[0043] The cell of the example 2 of a comparison is a cell using the thing of the same specification as the anode carbon layer of this operation gestalt as an anode carbon layer, respectively as the cathode carbon layer of this operation gestalt, and the thing of the same specification and a cathode carbon layer. That is, the cell of the example 2 of a comparison is a cell by which it was made for the direction of an anode carbon layer to become larger than the average pore diameter of a cathode carbon layer.

[0044] Drawing 3 shows aging of a cell electrical potential difference. It turns out that the cell of this operation gestalt excels the cell of the examples 1 and 2 of a comparison in the property of an electrical potential difference with the passage of time so that clearly from this drawing.

[0045] According to the polymer electrolyte fuel cell of this operation gestalt, thus, the average pore diameter of at least one porous layer which forms anode gas diffusion layer 1a By having made it smaller than the average pore diameter of the porous layer which forms cathode gaseous diffusion layer 1b The amount of the moisture relatively discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section of an anode with little moisture content decreases, and the amount of the moisture relatively discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section of a cathode with much moisture content increases.

[0046] Therefore, since the cell side interior division cloth of the moisture content of the electrode reaction section produced with time is eased, ununiformity-ization of the current density produced by lowering of the reaction area accompanying lowering of the diffusibility by condensation of the water locally generated in the cell reaction section and the electrolyte performance degradation by desiccation can be prevented, and the stability of cell voltage with the passage of time improves.

[0047] Moreover, according to the manufacture approach of the polymer electrolyte fuel cell of this operation gestalt, an average pore diameter becomes small rather than the porous layer to which the porous layer which touches a catalyst bed among anode gas diffusion layer 1a touches a catalyst bed among cathode gaseous diffusion layer 1b.

[0048] The 2nd operation gestalt of the [2nd operation gestalt] is the same as that of the configuration of the polymer electrolyte fuel cell of said 1st operation gestalt, and 90% or more of the pore of 1d of anode carbon layers and cathode carbon layer 1e consists of pores 10 micrometers or less. That is, 90% or more of the pore of the porous layer which touches a catalyst bed consists of pore diameters of 10 micrometers or less.

[0049] Next, an operation and effectiveness of this operation gestalt are explained.

[0050] About the cell of this operation gestalt, the generation-of-electrical-energy trial was performed at the operating temperature of 80 degrees C, operating pressure 0.1MPa, current density 400 mA/cm<sup>2</sup>, the anode humidification temperature of 70 degrees C, the cathode humidification temperature of 70 degrees C, 70% of rates of hydrogen gas utilization, and 40% of air gas utilization factors. Here, in order to compare with the cell of this operation gestalt, the cell which changed only the specification of a carbon layer was created and the generation-of-electrical-energy trial was performed on the same conditions. It is shown as an example of a comparison below.

[0051] What changed systematically the particle diameter of the carbon powder used as a cell of the example of a comparison in case a cathode carbon layer is formed was created. All specifications other than



a cathode carbon layer were unified. The rate that pore 10micron or less occupies by making the particle diameter of carbon powder increase was able to obtain the carbon layer which fell gradually.

[0052] The relation between the rate that pore 10 micrometers or less occupies to drawing 4 , and the amount of lowering of the cell electrical potential difference of 1000 hours after is shown. The fuel cell of this operation gestalt is understood that a property with the passage of time is better than the cell of the example of a comparison so that clearly from this drawing.

[0053] According to this operation gestalt, thus, 1d of anode carbon layers and cathode carbon layer 1e Since 90% or more constituted all from pore 10 micrometers or less, in the field where the relative humidity of reactant gas is low Since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section decreases and the amount of the moisture supplied to the electrode reaction section decreases in the field where the relative humidity of reactant gas is high, the field interior division cloth of the moisture content of the electrode reaction section produced with the field interior division cloth of the relative humidity of reactant gas is eased.

[0054] Therefore, ununiformity-ization of the current density produced by lowering of the reaction area accompanying lowering of the diffusibility by condensation of the water locally generated in the cell reaction section and the electrolyte performance degradation by desiccation can be prevented, and the stability of cell voltage with the passage of time improves.

[0055] The 3rd operation gestalt of the [3rd operation gestalt] is the same configuration as the polymer electrolyte fuel cell of said 1st operation gestalt, and the porosity of a gaseous diffusion layer is 70% or more. That is, the porosity of 1d of anode carbon layers and cathode carbon layer 1e is made into 70% or more.

[0056] Although the rate of the polytetrafluoroethylene (PTFE) which the carbon layer in the 1st operation gestalt is made to contain was made into 35% to sum total weight with carbon, as shown in drawing 5 , at 65% or less, the carbon layer from which porosity becomes 70% or more like the 1st operation gestalt is obtained.

[0057] Next, an operation and effectiveness of this operation gestalt are explained.

[0058] By making the porosity of 1d of anode carbon layers, and cathode carbon layer 1e 70% or more, lowering of the gaseous diffusion function of a gaseous diffusion layer can be prevented.

[0059] About the cell of this operation gestalt, the generation-of-electrical-energy trial was performed at the operating temperature of 80 degrees C, operating pressure 0.1MPa, current density 400 mA/cm<sup>2</sup>, the anode humidification temperature of 70 degrees C, the cathode humidification temperature of 70 degrees C, 70% of rates of hydrogen gas utilization, and 40% of air gas utilization factors. Here, in order to compare with the cell of this operation gestalt, the cell which changed only the specification of a carbon layer was created and the generation-of-electrical-energy trial was performed on the same conditions. It is shown as an example of a comparison below.

[0060] The cell on which porosity was reduced from 70% was created by making 70% the content of the polytetrafluoroethylene contained in a cathode carbon layer as a cell of the example of a comparison. Here, all of the specification of cells other than a cathode carbon layer were unified.

[0061] The relation between porosity and a cell electrical potential difference is shown in drawing 6 . As compared with the cell of the example of a comparison by which porosity is less than 70% by the cell of this operation gestalt, a cell electrical potential difference is high so that clearly from this drawing.

[0062] Thus, according to this operation gestalt, since the gaseous diffusion function of a gaseous diffusion layer can be prevented, a cell property improves.

[0063] The sectional view and drawing 8 which show the 4th operation gestalt of the polymer electrolyte fuel cell which [4th operation gestalt] drawing 7 requires for this invention are the perspective view showing the gaseous diffusion layer which constitutes the polymer electrolyte fuel cell by the 4th operation gestalt. In addition, the arrow head in drawing expresses the flow direction of reactant gas.

[0064] As shown in drawing 7 , anode gas diffusion layer 1a and cathode gaseous diffusion layer 1b consist of two-layer porous layers of carbon paper 1c (270 micrometers in thickness), and 1f of carbon layers.

[0065] 1f of this carbon layer is constituted from 1h of carbon layers with a large average pore diameter by the relative target which formed in the field of the one half of the reactant gas upstream as shown in drawing 8 and which formed in the field of 1g of carbon layers with a small average pore diameter, and the one half of the reactant gas downstream relatively. While 1g of carbon layers with a small average pore diameter is formed by the same specification as 1d of anode carbon layers of said 1st operation gestalt, 1h of porous layers with a large average pore diameter is formed by the same specification as cathode carbon layer 1e of said 1st operation gestalt.

[0066] Thus, with this operation gestalt, the average pore diameter of the part located in the reactant gas downstream of a gaseous diffusion layer is made larger than the average pore diameter of the part located in the reactant gas upstream section.

[0067] moreover, by the manufacture approach of the polymer electrolyte fuel cell of this operation gestalt To the field of objection of the field which joins catalyst bed 2a of a couple, and 2b to both sides of the solid-state polyelectrolyte film 3, and touches these catalyst bed 2a and the solid-state polyelectrolyte film 3 of 2b In the manufacture approach of the polymer electrolyte fuel cell which joins the gaseous diffusion layers 1a and 1b of the couple formed by the porous layer, into the part located in the reactant gas upstream section of the gaseous diffusion layers 1a and 1b After applying the ink which becomes a carbon porous body from a carbon particle and a fluorocarbon-resin-dispersion object at least so that a spreading side may touch a catalyst bed, While heat-treating and forming above the glass transition temperature of a fluororesin, into the part located in a reactant gas downstream After applying the fine particles which turn into a carbon porous body from a carbon particle and a fluororesin at least so that a spreading side may touch a catalyst bed, it has heat-treated and formed above the glass transition temperature of a fluororesin.

[0068] Next, an operation and effectiveness of this operation gestalt are explained.

[0069] In the polymer electrolyte fuel cell of this operation gestalt, since the reactant gas upstream section is relatively small, the pore diameter of the carbon layer which touches a catalyst bed as compared with a downstream The amount of the moisture discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section relatively located in the reactant gas upstream section with low relative humidity decreases. Since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer increases from the electrode reaction section relatively located in a reactant gas downstream with high relative humidity, the field interior division cloth of the moisture content of the electrode reaction section is controlled.

[0070] About the fuel cell of this operation gestalt, the generation-of-electrical-energy trial was performed at the operating temperature of 80 degrees C, operating pressure 0.1MPa, current density 400 mA/cm<sup>2</sup>, the anode humidification temperature of 70 degrees C, the cathode humidification temperature of 70 degrees C, 70% of rates of hydrogen gas utilization, and 40% of air gas utilization factors. Here, in order to compare with the cell of this operation gestalt, the cell which changed only the specification of a carbon layer was created and the generation-of-electrical-energy trial was performed on the same conditions. It is shown as examples 1 and 2 of a comparison below.

[0071] The cell of the example 1 of a comparison is a cell using the thing of the specification same as a carbon layer of an anode and a cathode as the anode carbon layer in said 1st operation gestalt. That is, the carbon layer formed in the field of the one half of the reactant gas upstream of the cell of this operation gestalt covers the whole surface, and the cell of the example 1 of a comparison is formed.

[0072] The cell of the example 2 of a comparison is a cell using the thing of the specification same as a carbon layer of an anode and a cathode as the cathode carbon layer in said 1st operation gestalt. That is, the carbon layer in which the cell of the example 2 of a comparison was formed to the field of the one half of the reactant gas downstream of the cell of this operation gestalt is formed over the whole surface.

[0073] Aging of a cel electrical potential difference is shown in drawing 9 . It turns out that the cell of this operation gestalt excels the cell of the example of a comparison in the property of an electrical potential difference with the passage of time so that clearly from this drawing.

[0074] Thus, according to this operation gestalt, the amount of the moisture discharged with reactant gas through a gaseous diffusion layer from the electrode reaction section relatively located in the reactant gas upstream section with low relative humidity decreases. Since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer increases from the electrode reaction section relatively located in a reactant gas downstream with high relative humidity, the field interior division cloth of the moisture content of the electrode reaction section produced with the field interior division cloth of the relative humidity of reactant gas is eased.

[0075] Therefore, ununiformity-ization of the current density produced by lowering of the reaction area accompanying lowering of the diffusibility by condensation of the water locally generated in the cell reaction section and the electrolyte performance degradation by desiccation can be prevented, and the stability of cell voltage with the passage of time improves.

[0076] The perspective view showing the cell layered product in the 5th operation gestalt of the polymer electrolyte fuel cell which [5th operation gestalt] drawing 10 requires for this invention, drawing 11 (a), and (b) are the sectional views showing the cell of the center section which constitutes a cell layered product, respectively, and both ends.

[0077] As shown in drawing 10 and drawing 11 (a), and (b), the polymer electrolyte fuel cell of this operation gestalt consists of a cell layered product 6 which carried out the laminating of the cells 4a and 4b which made the solid-state polyelectrolyte film 3 pinch the gaseous diffusion layers 1a and 1b through catalyst bed 2a and 2b through the separator 5 which supplies reactant gas, and a collecting electrode plate 9 arranged to the ends of this cell layered product 6.

[0078] Cell 4a located in a center section was created by the same approach as the thing of said 1st operation gestalt. On the other hand, nearest cell 4b is that the mean particle diameter of the carbon particle used in case the cathode carbon layer which explained cathode carbon layer 1j with said 1st operation gestalt is formed forms using what is about 5 times, and the average pore diameter of cathode carbon layer 1j increased it to the collecting electrode plate 9 located in the edge of the cell layered product 6.

[0079] In addition, cell 4b located in an edge is constituted like said 1st operation gestalt except [ all ] cathode carbon layer 1j.

[0080] Thus, with this operation gestalt, the average pore diameter of the porous layer which forms the gaseous diffusion layer of at least 1 cel located in the edge of the cell layered product 6 is made larger than the average pore diameter of the porous layer which forms the gaseous diffusion layer of the cel of the center section of the cell layered product 6.

[0081] Next, an operation and effectiveness of this operation gestalt are explained.

[0082] In the cel of the edge of the cell layered product 6, compared with the cel located in a center section by heat dissipation, temperature is low, and relative humidity becomes high. Therefore, in the cel of an edge, gaseous diffusion nature falls by condensation of water. According to the configuration of this operation gestalt, in the cel of the edge of the cell layered product 6, since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer increases from the electrode reaction section, gaseous diffusion nature improves.

[0083] The generation-of-electrical-energy trial was performed about the polymer electrolyte fuel cell of this operation gestalt, and the cel electrical potential difference of the cell which constitutes the layered product was measured. The trial with the same said of what made the cathode carbon layer of the cell located in the layered product edge of the polymer electrolyte fuel cell of this operation gestalt the same specification as the thing of a center section was performed for the comparison.

[0084] Drawing 12 shows distribution of the cell electrical potential difference which constitutes this operation gestalt. In addition, the laminating is carried out to order from what has a small cel number. Since lowering of the cell voltage by lowering of the gaseous diffusion nature conventionally seen by the cell of an edge had been improved so that clearly from this drawing, the cel electrical potential difference became almost equal.

[0085] Thus, according to this operation gestalt, in the cel of the edge of a layered product, since the amount of the moisture discharged with reactant gas through a gaseous diffusion layer increases from the electrode reaction section, lowering of the cell voltage by lowering of gaseous diffusion nature can be prevented.

[0086]

[Effect of the Invention] As explained above, according to this invention, by setting up the pore diameter of the gaseous diffusion layer of a polymer electrolyte fuel cell the optimal, ununiformity-ization of moisture content distribution of the cell reaction section generated with the field interior division cloth of the relative humidity of the reactant gas which had become a technical problem conventionally can be corrected, and the highly efficient polymer electrolyte fuel cell with which the electrical potential difference stabilized with time is obtained can be offered.

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[Translation done.]

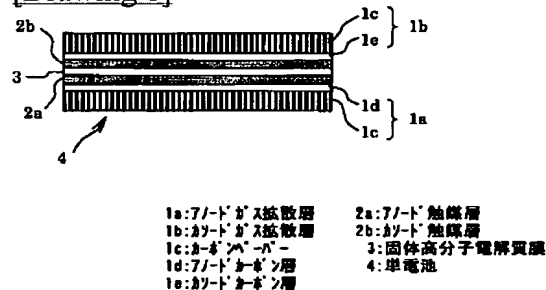
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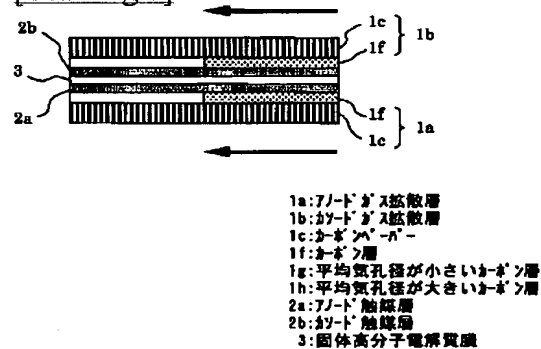
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3. In the drawings, any words are not translated.

## DRAWINGS

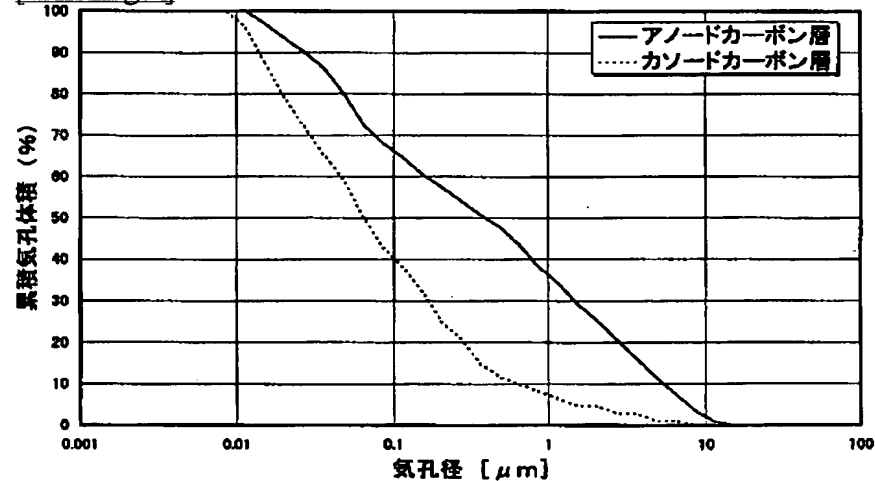
[Drawing 1]



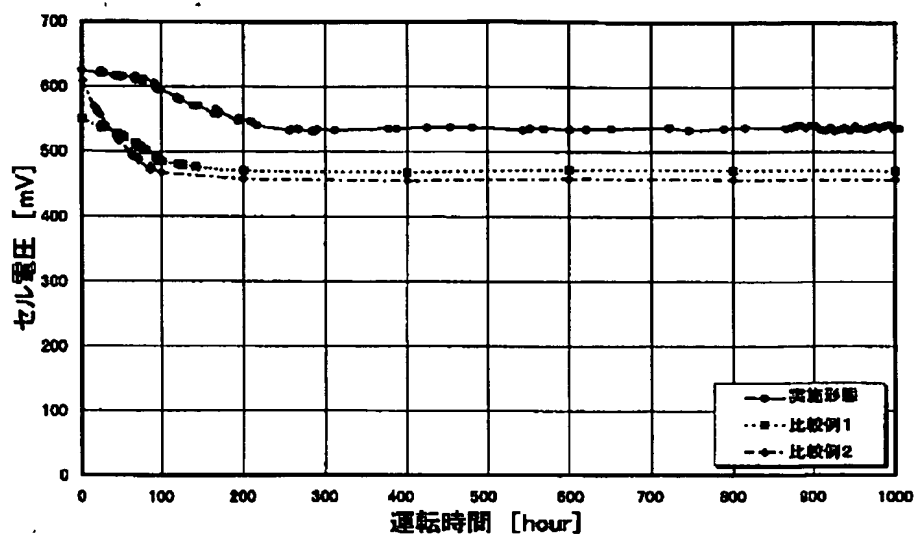
[Drawing 7]



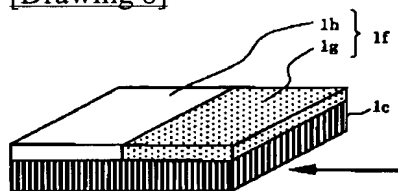
[Drawing 2]



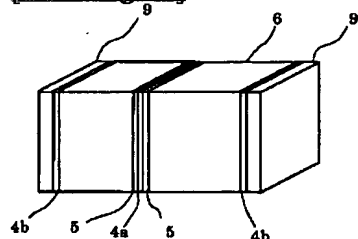
[Drawing 3]



[Drawing 8]

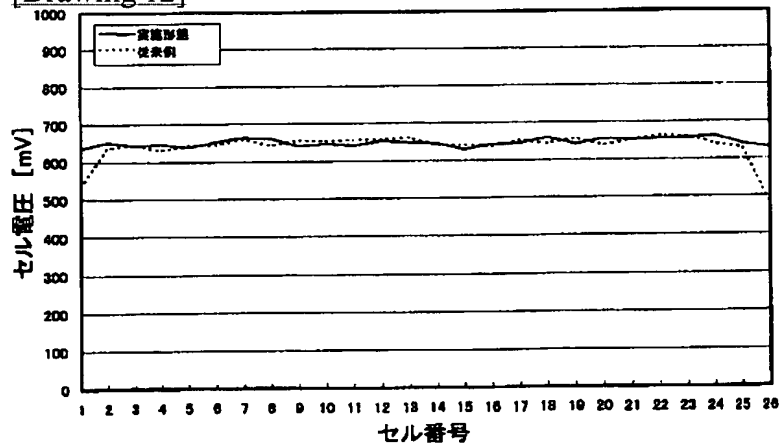


[Drawing 10]

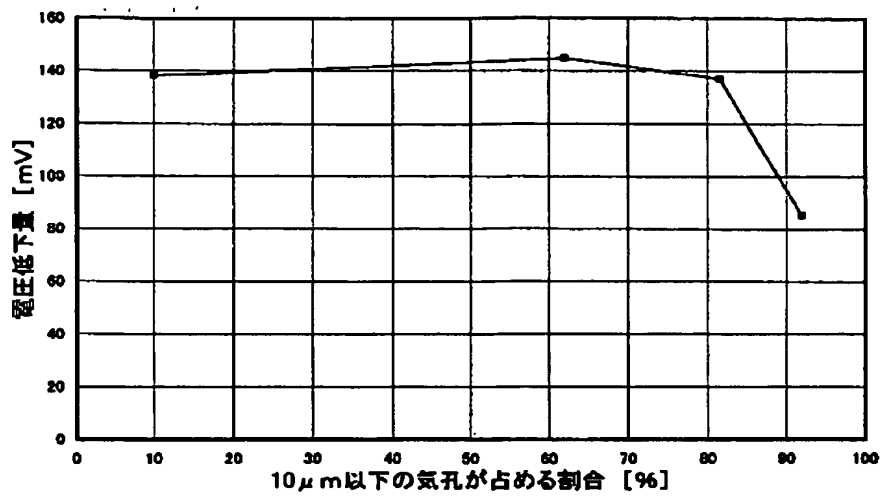


- 4a: 積層体中央部に位置する単電池  
 4b: 積層体端部に位置する単電池  
 5: セルリード  
 6: 単電池積層体  
 9: 集電板

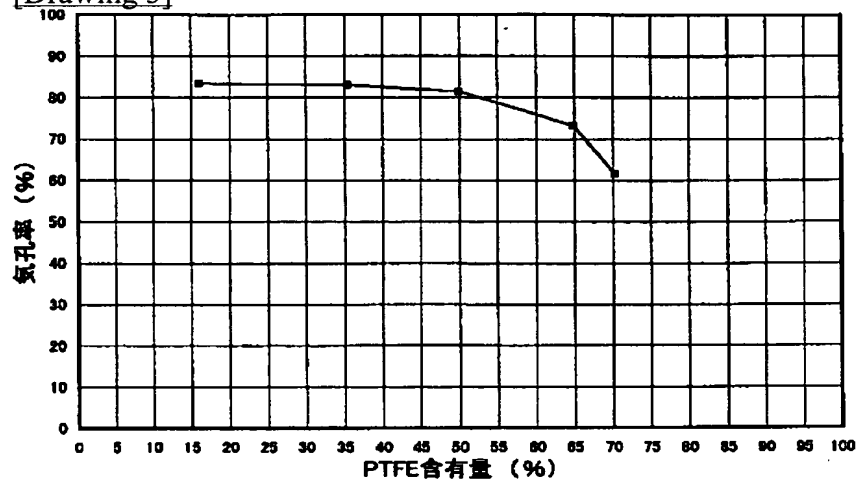
[Drawing 12]



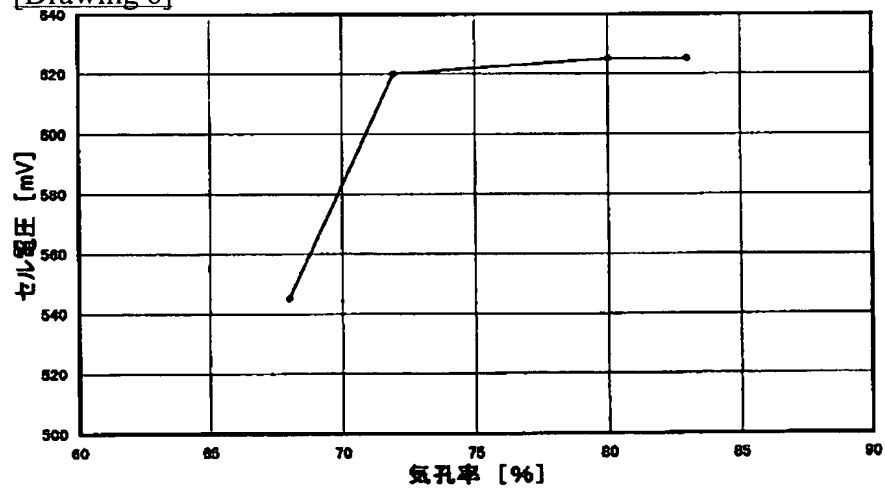
[Drawing 4]



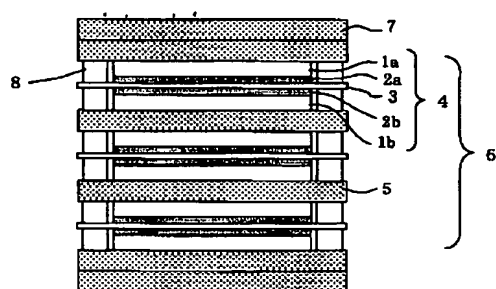
[Drawing 5]



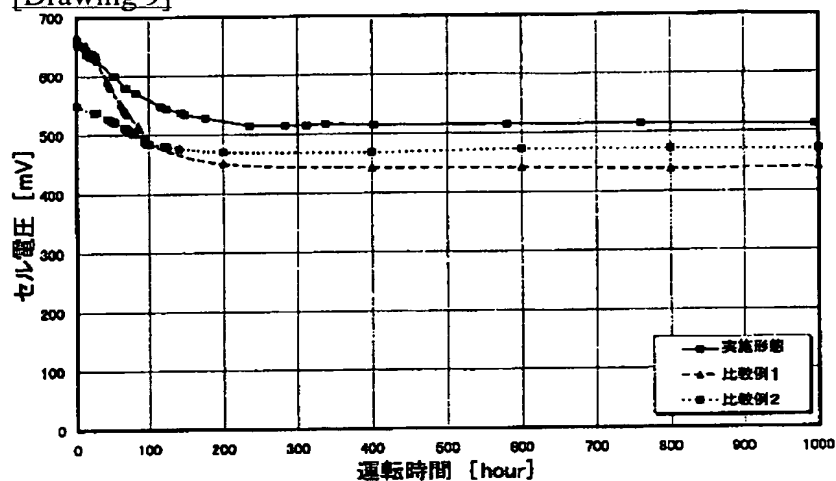
[Drawing 6]



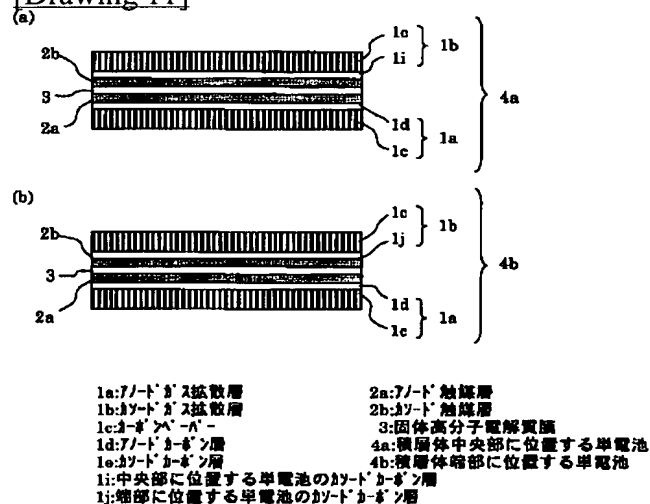
[Drawing 13]



[Drawing 9]



[Drawing 11]



[Translation done.]

## PATENT ABSTRACTS OF JAPAN

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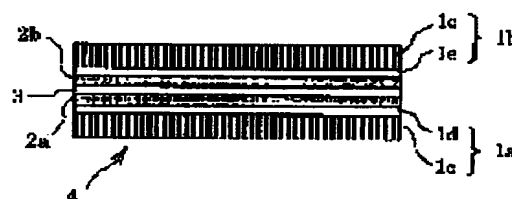
(72)Inventor : TOMOSAWA HIROSHI  
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## (54) SOLID POLYMER TYPE FUEL CELL AND MANUFACTURE THEREOF

## (57)Abstract:

**PROBLEM TO BE SOLVED:** To provide a voltage stable with age by correcting unevenness in contained water distribution.

**SOLUTION:** This fuel cell is provided with a solid polymer electrolyte membrane 3, an anode catalyst layer 2a and a cathode catalyst layer 2b placed on the both sides of the solid polymer electrolyte membrane 3, and an anode gas diffusion layer 1a and a cathode gas diffusion layer 1b individually placed on surfaces opposite to surfaces on which the catalyst layers 2a, 2b are in contact with the solid polymer electrolyte membrane 3. The average porous diameter of at least one porous layer forming the anode gas diffusion layer 1a is smaller than the average porous diameter of a porous layer forming the cathode gas diffusion layer 1b.



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## LEGAL STATUS

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decision of rejection]

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を流通させる冷却板7が介挿されている。

【0005】また、系外へのガスリークは、ガス利用率の低下や水素などの可燃ガスによる爆発の危険性があるため、固体高分子電解質膜3とセパレータ5との間にはシール部8を介してガスシールされている。

【0006】固体高分子電解質膜3には、例えばフッ素系イオン交換膜であるパーフルオロスルホン酸膜が用いられ、これらにより、電池の含水率が少なくなり、電池の導電性が悪化し、電池性能が低下する。一方、逆に電池の含水率が過剰になると、電池反応部で水が凝結し、電池反応部へのカスの供給が阻害されるため、同様にして電池性能が低下する。

【0007】ところで、カソードガス拡散膜1bでは、電極反応に伴って水が生成されるので、アノードガス拡散膜1aよりも含水量が多く、反応ガスの相対湿度も高い。また、カソードガス拡散膜1bで生成した水は、一部アノードガス拡散膜1aに移動し、これらの水分は反応ガスによって一部持ち出されるので、反応ガスの下流の方が上流と比較して相対湿度が高い。

【0008】すなわち、アノードガス拡散層1aとカソードガス拡散層1b、あるいは反応ガスの上流と下流とは、反応ガスの相対湿度に分布が生じている。このように電池平面内には生じている反応ガスの相対湿度の面内分布によって、電池平面内において触媒層や電解質膜といった電極反応部の含水量に面内分布が発生する。

【0009】その結果、含水量の過剰な部分では水の凝縮によってガス拡散性が悪化する一方、含水量の少ない部分では電解質棉線の低下に伴って反応表面積が低下するので、電流密度の面内不均一化が生じ、電池性能が低下する。

【0010】したがって、電池性能の低下を防ぐためには、反応ガスの上流および下流における相対湿度の分布が触媒層や電解質層の含水量の面内分布を引き起こさないようにする必要がある。その一例として、通常ガス拡散層に用いられている気孔径が大きいカーボン多孔質媒体の触媒層と接する面に、カーボン多孔質媒体よりも気孔径の小さい気孔の割合が多い層を設けることで、反応ガスの相対湿度の分布によって電解反応が行われる触媒層や電解質層の含水量に分布を生じさせないような緩衝材としての働きを持たせたものが提案されている。

【0011】

【説明が解決しようとする課題】しかしながら、上述した従来例において、長時間発電を行っているとき、アノードガス拡散層1aとカソードガス拡散層1bとの相対湿度の違い、あるいは反応ガスの上流と下流における相対湿度の違いに起因する反応ガスの相対湿度の面内分布によって、徐々に電極反応部でも電地面内における含水量

に分布が生じる。この電極反応部における含水量の電池電圧が低下すると、水の凝縮によるガス拡散性の低下および乾燥による電解質性能の低下に伴う反応面積の低下が生じて、電流密度の不均一化が発生するため、電池電圧が低下するという課題がある。

【0012】一方、燃料電池スタックでは、端部に位置するセルの方が放熱量が多いため、中央部に位置するセルよりも電池温度が低く相対湿度が高い。したがって、端部に位置するセルは、水の凝結によるガス拡散機能の低下により、中央部のセルよりも電池電圧が低いという課題もある。

【0013】そこで、本発明は上記問題を考慮してなされるものである。固体高分子型電池用のガス拡散層の気孔率を最適化すること、従来電解質を用いた反応ガス（水素）の相対湿度のすることによって生じ、かつ電池反応部の経時的に生じる含水分布の不均一化を是正することによらる。経時的に安定した電圧が得られる高性能な固体高分子型燃料電池およびその製造方法を提供することにある。

**【0014】**

【課題を解決するための手段】そこで、上記問題を解決するため、請求項1記載の固体高分子型燃料電池は、固体高分子電解質膜と、この固体高分子電解質膜の両面に配置したアノード触媒層およびカソード触媒層と、これら触媒層の前記固体高分子電解質膜に接する面の反対の面にそれぞれ配置されかつ多孔質で形成されたアノードガス拡散層およびカソードガス拡散層とを備えた固体高分子型燃料電池において、前記アノードガス拡散層は、前記アノードガス拡散層およびカソードガス拡散層は、前記アノードガス拡散層において、前記アノードガス拡散層を形成する少なくとも一つのも一つの多孔質孔径は、前記カソードガス拡散層を形成する多孔質層の平均気孔徑よりも小さいことを特徴とする。

【00015】請求項1記載の固体高分子型燃料電池の構成において、相対的に含水量の少ないアノードの電極反応反応層部分からガス拡散層を介して反応ガスとともに排出される水分の量は減少し、相対的に含水量の多いカソードの電極反応反応層部分からガス拡散層を介して反応ガスとともに排出される水分の量は増加するので、電極反応部の含水量の面内分布が抑制される。

【0016】請求項2記載の固体高分子型燃料電池は、固体高分子子電解質膜と、この固体高分子子電解質膜の両面に配置した一対の触媒層と、この触媒層の前記固体高分子子電解質膜と接する面の反対の面に設置された多孔質層と形成される一対のガス拡散層とを備えた固体高分子型燃料電池において、前記ガス拡散層の反応ガス下流部に位置する部分の平均孔径は、反応ガス上流部に位置する部分の平均孔径よりも大きいことを特徴とする。

【0017】請求項2記載の固体高分子型燃料電池の構成により、相対的に含水量の少ない反応ガス上流部では電極反応部からガス拡散層を介して反応ガスとともに排

出される水分の量は減少し、相対的に含水量の多い反応ガス下流部では電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は増加するので、電極反応部の含水量の面内分布が抑制される。

【T0018】請求項3記載の固体高分子型燃料電池は、固体高分子型電解質膜と、この固体高分子型電解質膜の両面に配置した一对の触媒膜と、前記固体高分子型電解質膜と接する面の反対の面に配置された多孔質膜で形成され、一对のガス拡散層とを有する電池を、反応ガス供給機能を有するガス不透過性セパレータを介して複数個の固体高分子型燃料電池として構成される固体高分子型燃料電池において、前記觸媒膜の端部に位置する少なくとも1セルのガス拡散層を形成する多孔質膜の平均気孔径は、前記觸媒膜の中央部のセルのガス拡散層を形成する多孔質膜の平均気孔径よりも大きく、この特徴とされる。

【0019】積層型端部のセルでは放熱により、中央部に位置するセルと比べて温度が低く、相対湿度が高くなる。よって、端部のセルでは水の蒸発により、ガス拡散性が低下する。請求項3記載の固体高分子型燃料電池の構造により、積層型端部のセルでは、電極反応部からガス拡散部を介して反応ガスと水とに排出される水分の量が増加するため、ガス拡散性が向上する。

【0020】請求項4記載の固体高分子型燃料電池は、請求項1ないし3のいずれかに記載の触媒層と接する多孔質層の気孔の90%以上が $10\mu\text{m}$ 以下の気孔徑で構成されることを特徴とする。

【0021】請求項4記載の固体素子型燃料電池の構成により、反応ガスと電極反応部の間で水分の移動量が減少するので、反応ガスの相対温度が低い領域では、電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量が減少し、反応ガスの相対温度が高い領域では、電極反応部に供給される水分の量が減少するので、反応ガスの相対温度の面内分布により生じる電極反応部の含水量の面内分布が緩和される。

【0022】請求項5記載の固体高分子型燃料電池は、請求項1ないし4のいずれかに記載の触媒層と接する多孔質の気孔率を70%以上にすることを特徴とする。

【0023】請求項5記載の固体高分子型燃料電池によれば、ガス拡散層のガス拡散機能の低下を防ぐことができる。

【0024】請求項6記載の固体高分子型燃料電池の製造方法は、固体高分子電解質膜の両面に7ノード触媒層およびカソード触媒層を接合し、これら触媒層の前記固体高分子電解質膜と接する面の反対の面にそれぞれ多孔質膜で被覆されるアノードガス拡散層およびカソードガス拡散層を接合する固体高分子型燃料電池の製造方法に比し、前記7ノード触媒層は、カーボン多孔質体状粒子とカーボン粒子とワックス樹脂分散体とからなるインクを塗布面が触媒層と接するようにならな、ワックス樹脂のガラス転移温度以上で熱処理し、形成する。

一方、前記カソードガス拡散層は、カーボン多孔質体中に少量なくともカーボン粒子とフッ素樹脂粒子とからなる影射を塗布面が融媒層と接するように塗布した後、フッ素樹脂のガラス転移温度以上で熱処理して形成することゝ特徴とする。

【0025】請求項6記載の固体高分子型燃料電池の製造方法によれば、アノードガス拡散層のうち触媒層と接する多孔質層は、カソード拡散層のうち触媒層と接する多孔質層よりも平均気孔径が小さくなる。

【0026】請求項7記載の固体高分子型燃料電池の製造方法は、請求項6記載のフッ素樹脂固形分の重量割合をカーボン粒子とフッ素樹脂固形分の合計重量に対して65%以下にすることを特徴とする。

【0027】請求項7記載の固体高分子型燃料電池の製造方法によれば、ガス拡散層の気孔率が70%以上になる。

**【0002】**請求項8記載の固体高分子型燃料電池の製造方法は、固体高分子電解質層の面に対しての触媒層を接合し、これら触媒層の前記固体高分子電解質層と接する面の反対面に、多孔質体で形成される一方のガス拡散板を取着を接合する。このようにして形成された燃料電池は、前記ガス拡散板の反応ガスを上流部に位置する部分に供給し、カーボン多孔質体に少なくともカーボン粒子とフッ素樹脂とが含有されているインクを塗布層が触媒層に接するように塗布した後、フッ素樹脂のガラス転移温度以上で熱処理して形成される。一方、反応ガス下流部に位置する部分には、カーボン・多孔質体に少なくともカーボン粒子とフッ素樹脂とが含有される粉体を塗布層が触媒層に接するように塗布した後、フッ素樹脂のガラス転移温度以上で熱処理して形成したことを特徴とする。

【0029】請求項8記載の固体高分子型燃料電池の製造方法によれば、ガス拡散層のうち触媒層と接する多子質層の反応ガス下流部に位置する部分は、反応ガス上流部に位置する部分よりも平均孔径が大きくなる。

【0030】

【発明の実施の形態】以下、本発明の実施形態を図面を参照して具体的に説明する。なお、従来の構成と同一または対応する部分には図13と同一の符号を用いて説明する。

【0031】第1実施形態）図1は本発明に係る固体高分子型燃料電池の第1実施形態を示す断面図である。

【0032】図1に示すように、固体高分子型燃料電池は、固体高分子電解質膜3と、この固体高分子電解質膜3の両面に配置したアノード触媒層2aおよびカソード触媒層2bと、これら触媒層2a、2bの固体高分子電解質膜3と接する面と反対の面にそれぞれ配置された多孔質層と形成されるアノードガス拡散層1aおよびカソードガス拡散層1bとで電極セル4が構成され、この電極セル4が構成された他の構成要素を省略する。

- 【0033】アノードガス拡散層1aは、カーボンペーパー1c（厚さ270 $\mu$ m）とカーボン層1dの2層の多孔質で構成される。このアノードカーボン層1dは、カーボン粒子（Vulcan XC-72R）、ポリテトラフルオロエチレン（分散体）（TFE 30）、界面活性剤および純水を混合したインクをスクリーンプリンターを用いてカーボンペーパー1c上に塗布した後、350℃で15分間熱処理を行い形成した。
- 【0034】一方、カソードガス拡散層1bは、カーボンペーパー1cとカソードカーボン層1eの2層の多孔質で構成される。このカソードカーボン層1eは、カーボン粒子（Vulcan XC-72R）およびポリテトラフルオロエチレン粉末（TFE 60）を混合した粉体をカーボンペーパー1c上に塗布した後、350℃で15分間熱処理を行い形成した。
- 【0035】図2はポリテトラフルオロエチレンの含有量を35%としたときの、アノードカーボン層1dおよびカソードカーボン層1eの気孔率分布を示したものである。アノードカーボン層1dよりもカソードカーボン層1eの方が気孔率が高いものの割合が多く、平均気孔率が大きくなくなっている。ここで、アノードカーボン層1dおよびカソードカーボン層1eはいずれも90%以上が10 $\mu$ m以下の気孔で構成されており、気孔率が約80%となるものが得られた。
- 【0036】次に、アノードカーボン層1dの上にアノード触媒層2aを、カソードカーボン層1e上にカソード触媒層2bをそれぞれ形成し、固体高分子型燃料電池3を保持させて接合し、上記のように単電池4を作成した。
- 【0037】このように本実施形態の固体高分子型燃料電池では、アノードガス拡散層1aを形成する少なくとも一つの多孔質層の平均気孔率を、カソードガス拡散層1bを形成する多孔質層の平均気孔率よりも小さくしてある。
- 【0038】以上のように、本実施形態の固体高分子型燃料電池の製造方法では、アノードガス拡散層1aは、カーボン多孔質体に少なくともカーボン粒子とフッ素樹脂分散体とからなるインクを塗布面が触媒層と接するよう処理して形成する一方、カソードガス拡散層1bは、カーボン多孔質体に少なくともカーボン粒子とフッ素樹脂粒子とからなる粉体を塗布面が触媒層と接するよう処理した後、フッ素樹脂のガラス転移温度以上で熱処理して形成している。
- 【0039】次に、本実施形態の作用および効果について説明する。
- 【0040】本実施形態の固体高分子型燃料電池では、アノードカーボン層1dの平均気孔率はカソードカーボン層1eの平均気孔率と比べて小さいので、含水量の少ないアノードの電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は増加する。
- 【0041】本実施形態の固体高分子型燃料電池について、運転温度80℃、運転圧力0.1MPa、電流密度4.00mA/cm<sup>2</sup>、アノード加湿温度70℃、カソード加湿温度70℃、水素ガス利用率70%、空気ガス利用率40%で発電率40%で発電試験を行った。ここで、本実施形態の電池と比較して、比較例1、2として示す。
- 【0042】比較例1の電池は、アノードカーボン層およびカソードカーボン層として、本実施形態におけるカソードカーボン層と同様の仕様のものを用いた電池である。すなわち、比較例1の電池はアノードおよびカソードの気孔率分布が等しくなるようにした電池である。
- 【0043】比較例2の電池は、アノードカーボン層として、本実施形態のカソードカーボン層と同様の仕様のもの、カソードカーボン層として、本実施形態のアノードカーボン層と同様の仕様のものをそれぞれ用いた電池である。すなわち、比較例2の電池はアノードカーボン層の方がカソードカーボン層の平均気孔率よりも大きくなるようにした電池である。
- 【0044】図3はセル電圧の経時変化を示したものである。この図から明らかなように、本実施形態の電池は比較例1、2の電池よりも電圧の経時特性が優れていることが判る。
- 【0045】このように本実施形態の固体高分子型燃料電池によれば、アノードガス拡散層1aを形成する少なくとも一つの多孔質層の平均気孔率を、カソードガス拡散層1bを形成する多孔質層の平均気孔率よりも小さくしたことにより、相対的に含水量の少ないアノードの電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は減少し、相対的に含水量の多いカソードの電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は増加する。
- 【0046】したがって、経時的に生じていた電極反応部の含水量の電池面内分布が緩和されるので、電池反応部で局所的に発生する水の凝縮による拡散性の低下および乾燥による電極性能の低下に伴う反応面積の低下に伴う電圧の経時安定性が向上する。
- 【0047】また、本実施形態の固体高分子型燃料電池の製造方法によれば、アノードガス拡散層1aのうねり、凹凸、接する多孔質層は、カソードガス拡散層1bのうねり、凹凸、接する多孔質層よりも平均気孔率が小さくなる。
- 【0048】【第2実施形態】第2実施形態は、前記第1実施形態の固体高分子型燃料電池の構成と同様であって、アノードカーボン層1dおよびカソードカーボン層1eの気孔の90%以上が10 $\mu$ m以下の気孔で構成されている。すなわち、触媒層と接する多孔質層の気孔の90%以上が10 $\mu$ m以下の気孔で構成されている。
- 【0049】次に、本実施形態の作用および効果について説明する。
- 【0050】本実施形態の電池について、運転温度80℃、運転圧力0.1MPa、電流密度4.00mA/cm<sup>2</sup>、アノード加湿温度70℃、カソード加湿温度70℃、水素ガス利用率70%、空気ガス利用率40%で発電試験を行った。ここで、本実施形態の電池と比較して、比較例3として示す。
- 【0051】比較例3の電池は、アノードカーボン層を形成する際に用いるカーボン粒子の粒径を系統的に変えたものを作成した。カソードカーボン層以外の仕様のものは比較例1の仕様のものと同一である。
- 【0052】図4に10 $\mu$ m以下の気孔が占める割合と、10.00時間後のセル電圧の低下量との関係を示す。この図から明らかなように、本実施形態の燃料電池は、経時特性が比較例の電池よりも良好であることが判る。
- 【0053】このように本実施形態によれば、アノードカーボン層1dおよびカソードカーボン層1eは、いずれも90%以上が10 $\mu$ m以下の気孔で構成したので、反応ガスの相対湿度が低い領域では、電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量が減少し、反応ガスの相対湿度が高い領域では、電極反応部に供給される水分の量が減少するので、反応ガスの相対湿度の面内分布により生じる電極反応部の含水量の面内分布が緩和される。
- 【0054】よって、電池反応部で局所的に発生する水の凝縮による拡散性の低下および乾燥による電極性能の低下に伴う反応面積の低下に伴う電圧の経時安定性が向上する。
- 【0055】【第3実施形態】第3実施形態は、前記第1実施形態の固体高分子型燃料電池と同様に構成であって、ガス拡散層の気孔率が70%以上である。つまり、アノードカーボン層1dおよびカソードカーボン層1eの気孔率を70%以上としたものである。
- 【0056】第1実施形態におけるカーボン層に含有させるポリテトラフルオロエチレン（PTFE）の割合はカーボンとの合計重量に対して35%としたが、図5に示すように65%以下では、第1実施形態と同様に気孔率が70%以上となるカーボン層が得られる。
- 【0057】次に、本実施形態の作用および効果について説明する。
- 【0058】アノードカーボン層1dおよびカソードカーボン層1eの気孔率を70%以上にすることで、ガス拡散層のガス拡散性能の低下を防ぐことができる。
- 【0059】本実施形態の電池について、運転温度80℃、運転圧力0.1MPa、電流密度4.00mA/cm<sup>2</sup>、アノード加湿温度70℃、カソード加湿温度70℃、水素ガス利用率70%、空気ガス利用率40%で発電試験を行った。ここで、本実施形態の電池と比較して、比較例4として示す。
- 【0060】比較例4の電池として、カソードカーボン層中に含まれるポリテトラフルオロエチレンの含有量を70%にすることで、気孔率を70%より低下させた電池を作成した。ここで、カソードカーボン層以外の仕様の仕様のものは比較例1の仕様のものと同一である。
- 【0061】図6に気孔率とセル電圧との関係を示す。この図から明らかなように、本実施形態の電池では、気孔率が70%を下回る比較例の電池と比較してセル電圧が高い。
- 【0062】このように本実施形態によれば、ガス拡散層のガス拡散性能を防ぐことができるので、セル特性が向上する。
- 【0063】【第4実施形態】図7は本発明に係る固体高分子型燃料電池の第4実施形態を示す断面図。図8は第4実施形態による固体高分子型燃料電池を構成するガス拡散層を示す斜視図である。なお、図中の矢印は反応ガスの流れの向きを表したものである。
- 【0064】図7に示すように、アノードガス拡散層1aおよびカソードガス拡散層1bは、カーボンペーパー1c（厚さ270 $\mu$ m）とカーボン層1fの2層の多孔質で構成される。
- 【0065】このカーボン層1fは、図8に示すように反応ガス上流側の半分の面に形成した相対的に平均気孔率の小さいカーボン層1gと、反応ガス下流側の半分の面に形成した相対的に平均気孔率の大きいカーボン層1hとで構成される。平均気孔率の小さいカーボン層1gは、前記第1実施形態のアノードカーボン層1dと同様の仕様の仕方で形成されている。
- 【0066】このように本実施形態では、ガス拡散層の反応ガス下流部に位置する部分の平均気孔率を、反応ガス上流部に位置する部分の平均気孔率よりも大きくしてある。
- 【0067】また、本実施形態の固体高分子型燃料電池の製造方法では、固体高分子型燃料電池の面内の一対の触媒層2a、2bを接合し、これら触媒層2a、2bの

固体高分子電解質膜3と接する面の反対の面に、多孔質層で形成される一対のガス拡散層1a、1bを接合する。固体高分子燃料電池の製造方法において、ガス拡散層1a、1bの反応ガス上流部に位置する部分は、カーボン多孔質体に少なくともカーボン粒子とフッ素樹脂成分とからなるインクを塗布面が触媒層に接するように塗布した後、フッ素樹脂のガラス転移温度以上で熱処理して形成する一方、反応ガス下流部に位置する部分は、カーボン多孔質体に少なくともカーボン粒子とフッ素樹脂とからなる粉体を塗布面が触媒層に接するように塗布した後、フッ素樹脂のガラス転移温度以上で熱処理して形成してある。

【0068】次に、本実施形態の作用および効果について説明する。

【0069】本実施形態の固体高分子燃料電池では、反応ガス上流部は下流部と比較して、触媒層と接するカーボン層の気孔径が相対的に小さいので、相対的に相対湿度の低い反応ガス上流部に位置する電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は減少し、相対的に相対湿度の高い反応ガス下流部に位置する電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は増加するので、電極反応部の含水量の面内分布が抑制される。

【0070】本実施形態の燃料電池について、運転温度80℃、運転圧力0.1MPa、電流密度400mA/cm<sup>2</sup>、アノード加熱温度70℃、カソード加熱温度70℃、水素ガス利用率70%、空気ガス利用率40%で発電試験を行った。ここで、本実施形態の電池と比較するため、カーボン層の仕様のみの変更した電池を作成し、同様な条件で発電試験を行った。以下比較例1、2として示す。

【0071】比較例1の電池は、アノードおよびカソードのカーボン層として、前記第1実施形態におけるアノードカーボン層と同様の仕様のものを用いた電池である。すなわち比較例1の電池は本実施形態の電池の反応ガス上流側の半分の面に形成したカーボン層が全面に亘って形成されたものである。

【0072】比較例2の電池は、アノードおよびカソードのカーボン層として、前記第1実施形態におけるカソードカーボン層と同様の仕様のものを用いた電池である。すなわち、比較例2の電池は本実施形態の電池の反応ガス下流側の半分の面に形成したカーボン層が全面に亘って形成されたものである。

【0073】図9にはセル電圧の経時変化を示したものである。この図から明らかなように、本実施形態の電池は比較例の電池よりも電圧の経時特性が優れていることが判る。

【0074】このように本実施形態によれば、相対的に相対湿度の低い反応ガス上流部に位置する電極反応部からガス拡散層を介して反応ガスとともに排出される水分

の量は減少し、相対的に相対湿度の高い反応ガス下流部に位置する電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量は増加するので、反応ガスの相対湿度の面内分布により生じる電極反応部の含水量の面内分布が緩和される。

【0075】よって、電極反応部で局所的に発生する水の凝結による拡散性の低下および乾燥による電解質性能の凝結に伴う反応面積の低下によって生じる電流密度の不均一化を防ぐことができ、電池電圧の経時安定性が向上する。

【0076】【第5実施形態】図10は本発明に係る固体高分子燃料電池の第5実施形態における単電池積層体を示す斜視図。図11(a)、(b)は、それぞれ単電池積層体を構成する中央部および両端部の単電池を示す断面図である。

【0077】図10および図11(a)、(b)に示すように、本実施形態の固体高分子燃料電池は、ガス拡散層1a、1bを触媒層2a、2bを介して固体高分子電解質膜3を挟持させた単電池4a、4bを反応ガスと供給するセパレータ5を介して積層した単電池積層体6と、この単電池積層体6の両端に配置した集電板9とで構成される。

【0078】中央部に位置する単電池4aは、前記第1実施形態のものと同様な方法で作成した。一方、単電池積層体6の両端部に位置する集電板9に最も近接する単電池4bは、カソードカーボン層1jを前記第1実施形態で説明したカソードカーボン層を形成する際に用いるカーボン粒子の平均気孔径が約5倍のものを使用して形成することで、カソードカーボン層1jの平均気孔径が増加した。

【0079】なお、端部に位置する電池4bは、カソードカーボン層1j以外は全て前記第1実施形態と同様に構成されている。

【0080】このように本実施形態では、単電池積層体6の端部に位置する少なくとも1セルのガス拡散層を形成する多孔質層の平均気孔径は、単電池積層体6の中央部のセルのガス拡散層を形成する多孔質層の平均気孔径よりも大きくしてある。

【0081】次に、本実施形態の作用および効果について説明する。

【0082】単電池積層体6の端部のセルでは、放熱により中央部に位置するセルと比べて温度が低く、相対湿度が高くなる。したがって、端部のセルでは水の凝結によりガス拡散性が低下する。本実施形態の構成によれば、単電池積層体6の端部のセルでは、電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量が向上する。ガス拡散性が向上する。

【0083】本実施形態の固体高分子燃料電池について発電試験を行い、積層体を構成している単電池のセル電圧を測定した。比較のため、本実施形態の固体高分子

燃料電池の積層体端部に位置する単電池のカソードカーボン層を、中央部のものと同一仕様にしたものについても同様な試験を行った。

【0084】図12は本実施形態を構成する単電池電圧の分布を示したものである。なお、セル番号の小さいものから順に積層している。この図から明らかなように、従来の電池でみられたガス拡散性の低下による電池電圧の低下が改善されるので、セル電圧がほぼ等しくなった。

【0085】このように本実施形態によれば、積層体の端部のセルでは電極反応部からガス拡散層を介して反応ガスとともに排出される水分の量が増加するため、ガス拡散性の低下による電池電圧の低下を防止することができ、

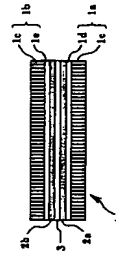
【0086】【発明の効果】以上説明したように、本発明によれば、固体高分子燃料電池のガス拡散層の気孔径を最適に設定することにより、従来課題となっていた反応ガスの相対湿度の面内分布によって発生する電池反応部の含水量の不均一化を是正することができ、経時的に安定した電圧が得られる高性能な固体高分子燃料電池を提供することができる。

【図面の簡単な説明】  
【図1】本発明に係る固体高分子燃料電池の第1実施形態を示す断面図。  
【図2】第1実施形態においてアノードカーボン層およびカソードカーボン層の気孔径分布を示す図。  
【図3】第1実施形態においてセル電圧の経時変化を示す図。

【図4】本発明の第2実施形態において10μm以下の気孔が占める割合とセル電圧の低下量との関係を示す図。  
【図5】本発明の第3実施形態においてPTFEと気孔率との関係を示す図。  
【図6】本発明の第3実施形態において気孔率とセル電圧との関係を示す図。

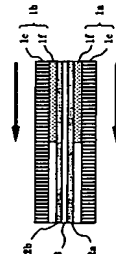
【図7】本発明の第3実施形態において気孔率とセル電圧との関係を示す図。

【図1】



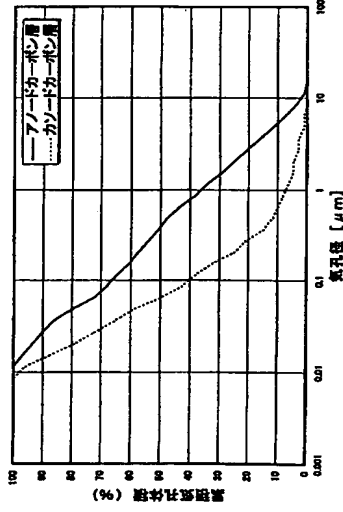
1a アノードガス拡散層  
1b カソードガス拡散層  
1c カソードカーボン層  
1d アノードカーボン層  
1e カソードカーボン層  
1f カソードカーボン層  
1g 平均気孔径の小さいカーボン層  
1h 平均気孔径の大きいカーボン層  
1i 中央部に位置する単電池のカソードカーボン層  
1j 端部に位置する単電池のカソードカーボン層  
2a アノード触媒層  
2b カソード触媒層  
3 固体高分子電解質膜  
4 単電池  
4a 積層体中央部に位置する単電池  
4b 積層体端部に位置する単電池  
5 セパレータ  
6 単電池積層体  
7 冷却板  
8 シール材  
9 集電板

【図7】

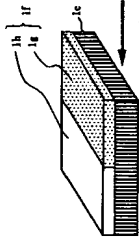


1a アノードガス拡散層  
1b カソードガス拡散層  
1c カソードカーボン層  
1d アノードカーボン層  
1e カソードカーボン層  
1f カソードカーボン層  
1g 平均気孔径の小さいカーボン層  
1h 平均気孔径の大きいカーボン層  
1i 中央部に位置する単電池のカソードカーボン層  
1j 端部に位置する単電池のカソードカーボン層  
2a アノード触媒層  
2b カソード触媒層  
3 固体高分子電解質膜  
4 単電池  
4a 積層体中央部に位置する単電池  
4b 積層体端部に位置する単電池  
5 セパレータ  
6 単電池積層体  
7 冷却板  
8 シール材  
9 集電板

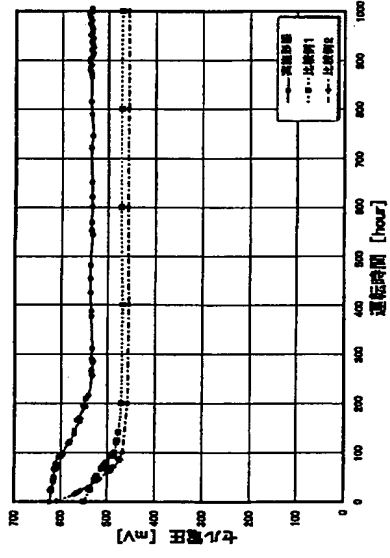
【図2】



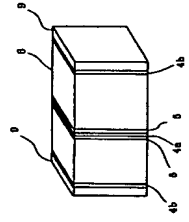
【図8】



【図3】

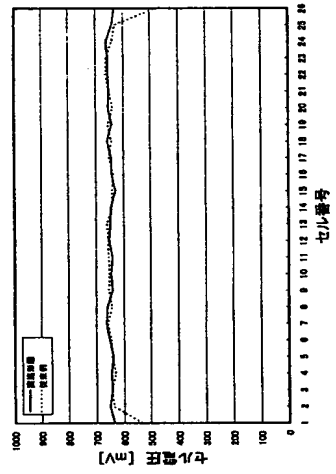


【図10】

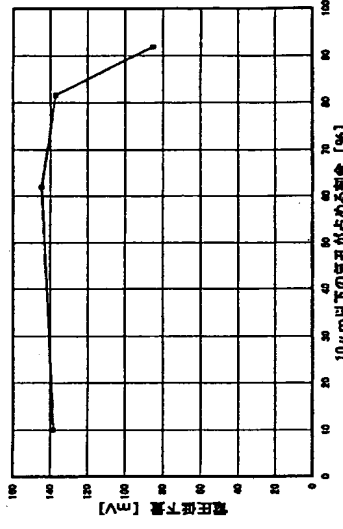


1. 図10は、図1の構造に示すように、  
多孔質材料と多孔質材料とを  
交互に積層した構造を示す。  
1a: 多孔質材料  
1b: 多孔質材料  
1c: 多孔質材料  
1d: 多孔質材料

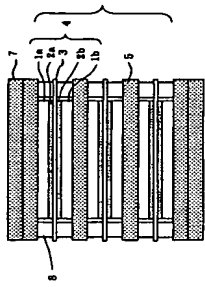
【図12】



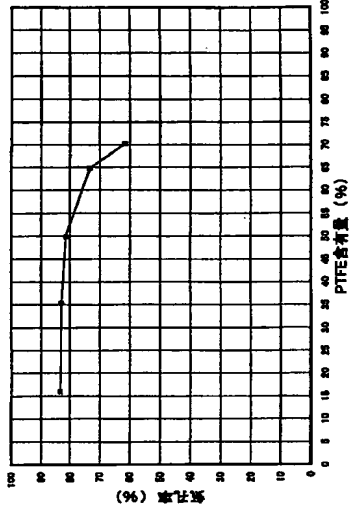
【図4】



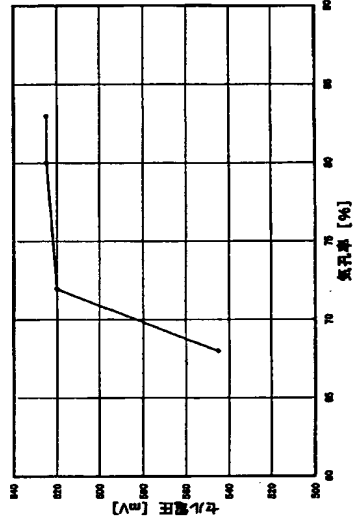
【図13】



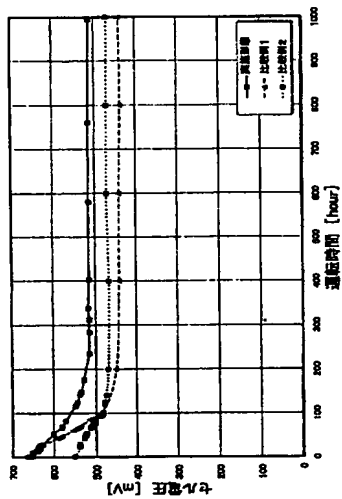
【図5】



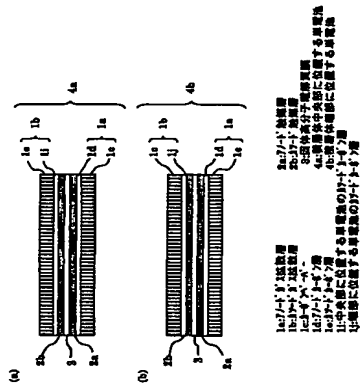
【図6】



【図9】



【図11】



フロントページの続き

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